

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Process for the removal of Acetylene Hydrocarbons and Butadiene from Gaseous Mixtures

We, FARBERWERKE HOECHST AKTIENGESELLSCHAFT vormals Meister Lucius & Brüning, a body corporate recognised under German law, of Frankfurt(M)-Höchst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It has been proposed to remove acetylene hydrocarbons from gaseous mixtures containing hydrogen and olefines by subjecting the gaseous mixture to the action of a palladium catalyst without converting an appreciable amount of the olefines into saturated hydrocarbons. The removal of the acetylene hydrocarbons must be carried out at a certain temperature and within a relatively short residence time, as a longer residence time would increase the quantity of olefines converted into saturated hydrocarbons and therefore the loss of olefines.

The present invention is based on the observation that acetylene hydrocarbons and butadiene can be removed simultaneously from gaseous mixtures containing hydrogen and olefines without an appreciable amount of saturated hydrocarbons being formed from the olefines present in the gaseous mixture, even if the latter contains a large excess of hydrogen, by passing the gaseous mixture at a temperature within the range of 150° C. to 300° C. over a catalyst containing on silica gel as carrier less than 1% by weight of palladium at a rate of 150 to 500 litres (measured at NTP) per litre of catalyst per hour. The catalyst advantageously contains at least 0.005% by weight, and preferably from about 0.01 to 0.1% by weight. Under the aforesaid conditions not only are the acetylene and higher acetylenes, such as diacetylene, methyl-acetylene, dimethyl-acetylene, ethyl-acetylene and vinyl-acetylene, removed from the gaseous mixture but also the butadiene, and allene is selectively hydro-

genated to propylene. It could not have been foreseen that this selective removal of the aforesaid compounds from the gaseous mixture, which results principally in the formation of the corresponding olefinically unsaturated hydrocarbons and little formation of other compounds, would take place because a considerable increase in the formation of saturated hydrocarbons would have been expected in view of the longer residence time which is characteristic of the process of this invention. It has been unexpectedly found that even when the quantity of catalyst is doubled, whereby the residence time is also doubled, the formation of saturated hydrocarbons is substantially avoided.

If a carrier other than silica gel were used, for example, pumice or aluminium oxide, and these carriers were charged with the aforesaid small proportion of palladium, such a catalyst would have a considerably shorter life. The selectivity of the catalyst would decrease if its noble metal content were increased beyond 1% by weight, that is the hydrogenation of the acetylenes and butadiene would not stop at the formation of monoolefines, especially ethylene and butylene, but complete hydrogenation to saturated hydrocarbons, such as ethane and butane, would occur. If the proportion of the palladium were less than 0.001% by weight, the activity of the catalyst would decrease considerably and would not enable acetylenes and butadiene to be removed from the gaseous mixture as desired.

In the process of this invention the gaseous mixture is passed over the catalyst at the rate of 150 to 500, and preferably 200–400, litres (measured at N.T.P.) per litre of catalyst per hour. The rate at which the gaseous mixture is passed over the catalyst is of decisive importance in the process of this invention. At rates lower than those specified the formation of saturated hydrocarbons increases. At higher rates, that is to say, at

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shorter residence times, the butadiene cannot be removed to the desired extent. Generally speaking, high rates are used at high temperatures and low rates at low temperatures, but always within the ranges specified above, that is to say, the rate may be higher the higher the temperature. Furthermore, it is of advantage to use a longer residence time, i.e., a lower rate of supply of the gaseous mixture within ranges specified above, the lower the concentration of the palladium in the catalyst.

A very advantageous method of carrying out the process is to bring the gaseous mixture to be freed from acetylene hydrocarbons and butadiene into contact with the catalyst in a reactor, for example, a cylindrical reactor, in which the catalyst is arranged in horizontal layers. The reactor is advantageously provided with means for heating and cooling the gaseous mixture in order to ensure maintenance of the reaction temperature. When the gaseous mixture to be treated contains an average of 2—4% of acetylenes and butadiene the heat liberated by the hydrogenation suffices to make good the loss of heat. If the gaseous mixture has a higher concentration of acetylenes and butadiene, cooling is necessary in order to maintain the

reaction temperature, and this is advantageously brought about by directing steam or softened water on the horizontal catalyst layers. An additional heat, which is necessary when the gaseous mixture contains less than 2% of the aforesaid substances, is advantageously supplied by preheating the gaseous mixture.

The composition of the gaseous mixture may vary within wide limits. Components, such as carbon monoxide or carbon dioxide, which are nearly always present in gases produced by cracking, do not impair the activity of the catalyst, but pronounced catalyst poisons, such as sulphur compounds, must be removed before the gaseous mixture enters the reactor. At an average content of acetylene hydrocarbons of 2—3% and of butadiene of 1.5—2% it is possible to pass 500 cubic metres of gaseous mixture through one litre of catalyst without an appreciable reduction in the activity of the palladium catalyst.

When, after a long period of use, it is found that the activity of catalyst has decreased, the catalyst can be regenerated in simple manner by first calcining it with oxygen or air and then treating it with hydrogen.

The following Examples illustrate the invention:

## EXAMPLE 1

400 litres (measured at N.T.P.) of a gaseous mixture composed of

$H_2$	25.7% by volume
$C_2H_6$	2.4% by volume
$C_2H_4$	63.8% by volume
$C_3H_2$	2.6% by volume
$C_4H_6$ (butadiene)	5.5% by volume

were passed into a reaction tube per hour at 150—200° C. over 1.5 litres of a palladium-silica gel catalyst (bulk density: about 0.5) containing 0.15 gram of palladium per litre (corresponding to about 0.03%).

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The gaseous mixture leaving the reaction tube had the following composition:

$H_2$	19.6% by volume
$C_2H_4$	3.2% by volume
$C_2H_6$	71.5% by volume
$C_2H_2$	0.0% by volume
$C_4H_6$ (butadiene)	0.1% by volume
$C_4H_8$	5.6% by volume

## EXAMPLE 2

120 cubic metres (measured at N.T.P.) of a gaseous mixture composed of:

CO	1.9% by volume
$N_2$	5.2% by volume
$H_2$	37.5% by volume
$CH_4$	16.2% by volume
$C_2H_2$ + Homologues	2.8% by volume
$C_2H_4$	22.3% by volume
$C_2H_6$	1.8% by volume
$C_3H_8$	7.0% by volume
$C_3H_6$	0.2% by volume
$C_4H_6$ (butadiene)	1.2% by volume
$C_4H_8$	1.8% by volume
$C_5H_{10}$	0.4% by volume
$C_5$ and higher hydrocarbons	1.7% by volume

were passed per hour at 220° C. over a total of 360 litres of the catalyst described in Example 1, which catalyst was distributed between two successive reaction zones.

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The gaseous mixture leaving the second reaction zone had the following composition:

CO	2.1% by volume
N <sub>2</sub>	4.9% by volume
H <sub>2</sub>	35.4% by volume
CH <sub>4</sub>	15.3% by volume
C <sub>2</sub> H <sub>2</sub> + homologues	—
C <sub>2</sub> H <sub>4</sub>	25.6% by volume
C <sub>2</sub> H <sub>6</sub>	2.2% by volume
C <sub>3</sub> H <sub>8</sub>	8.1% by volume
C <sub>3</sub> H <sub>6</sub>	0.1% by volume
C <sub>4</sub> H <sub>6</sub> (butadiene)	0.2% by volume
C <sub>4</sub> H <sub>8</sub>	3.3% by volume
C <sub>4</sub> H <sub>10</sub>	0.4% by volume
C <sub>5</sub> and higher hydrocarbons	2.4% by volume

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## EXAMPLE 3

400 litres (measured at N.T.P.) of a gaseous mixture composed of:

$N_2$	0.40
$CO_2$	10.70
CO	2.40
$H_2$	22.00
$CH_4$	21.10
$C_2H_6$	1.90
$C_3H_8$	25.30
$C_4H_{10}$ + homologues	4.00
$C_5H_{12}$	0.11
$C_6H_{14}$	6.00
allene	0.11
$C_4H_{10}$	0.30
$C_4H_8$	1.5
butadiene	1.00
$C_6$ + homologues	3.63
	100.—

were passed over a catalyst as used in Example 1. The hydrogenation temperature was 200° C. The gaseous mixture leaving the reaction zone had the following composition:

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$N_2$	0.50
$CO_2$	11.40
CO	2.60
$H_2$	16.80
$CH_4$	22.70
$C_2H_6$	4.00
$C_3H_8$	27.50
$C_4H_{10}$ + homologues	—
$C_5H_{12}$	0.18
$C_6H_{14}$	6.84
allene	—
$C_7H_{16}$	0.32
$C_8H_{18}$	2.57
butadiene	—
$C_9$ + homologues	4.59
	100.—

## WHAT WE CLAIM IS:—

1. A process for the removal of acetylene hydrocarbons and butadiene present in gaseous mixtures containing hydrogen and olefines, wherein the gaseous mixture is passed over a palladium-silica gel catalyst containing less than 1 per cent by weight of palladium at a temperature within the range of 150° C. to 300° C. and at a rate of 150 to 500 litres (measured at N.T.P.) per litre of catalyst per hour.

2. A process as claimed in claim 1, wherein the gaseous mixture is passed over the catalyst at the rate of 200 to 400 litres (measured at N.T.P.) per litre of catalyst per hour.

3. A process as claimed in claim 1 or claim 2, wherein the catalyst contains at least 0.005 per cent by weight of palladium.

4. A process as claimed in claim 1 or claim 2, wherein the catalyst contains a proportion of palladium within the range of 0.01 to 0.1 per cent by weight.

5. A process as claimed in any one of claims 1 to 4, wherein the gaseous mixture also contains allene and the allene is likewise

removed by the treatment.

6. A process as claimed in any one of claims 1 to 5, wherein a relatively high temperature within the said range and a relatively high rate of supply of the gaseous mixture within the said ranges are used.

7. A process as claimed in any one of claims 1 to 6, wherein the catalyst has a relatively low content of palladium and a relatively low rate of supply of the gaseous mixture within the said ranges is used.

8. A process for the removal of acetylene hydrocarbons and butadiene from a gaseous mixture containing hydrogen and olefines, conducted substantially as described in any one of the Examples herein.

9. Gaseous mixtures from which acetylene hydrocarbons and butadiene have been removed by the process claimed in any one of claims 1 to 8.

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